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Heterogeneous catalysis in oxidation of lignin model compounds

M. Melián-Rodríguez¹, S. Saravanamurugan¹, S. Kegnæs¹ and A. Riisager^{1*}

Introduction

Many different reactions and processes to convert biomass into high-value products and fuels have been proposed in the literature, giving special attention to the conversion of lignocellulosic biomass, which does not compete with food resources and is widely available as a low cost feedstock.

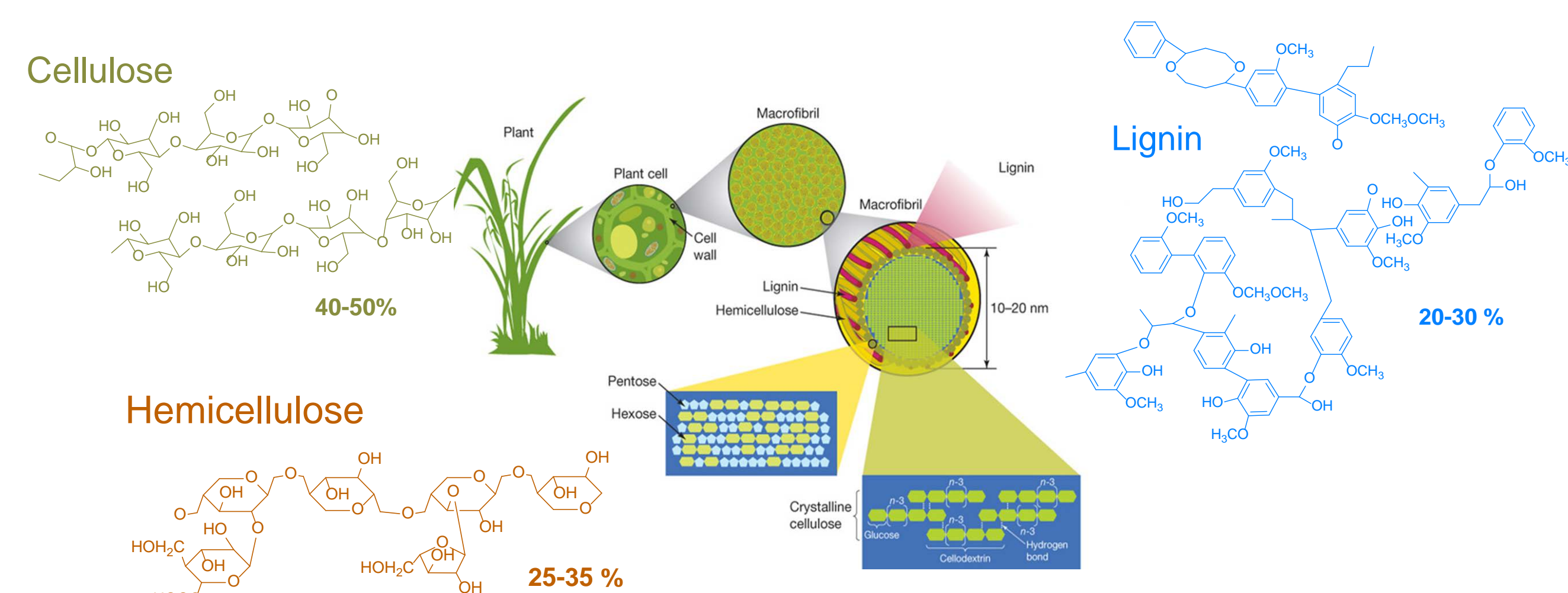


Figure 1. View of the role of lignin, cellulose and hemicellulose in a typical plant.

Lignin constitutes up to 40% of the heating value of lignocellulosic biomass. It is the most complex fraction and is harder to process compared to the sugar fractions.

Linkage type	Softwood lignin Total linkages (%)	Hardwood lignin Total linkages (%)
β -O-4	45-50	60
5-5	19-22	9
β -5	9-12	6
β -1	7-9	7
α -O-4	6-8	-
4-O-5	4-7	6,5
β - β	2-4	3

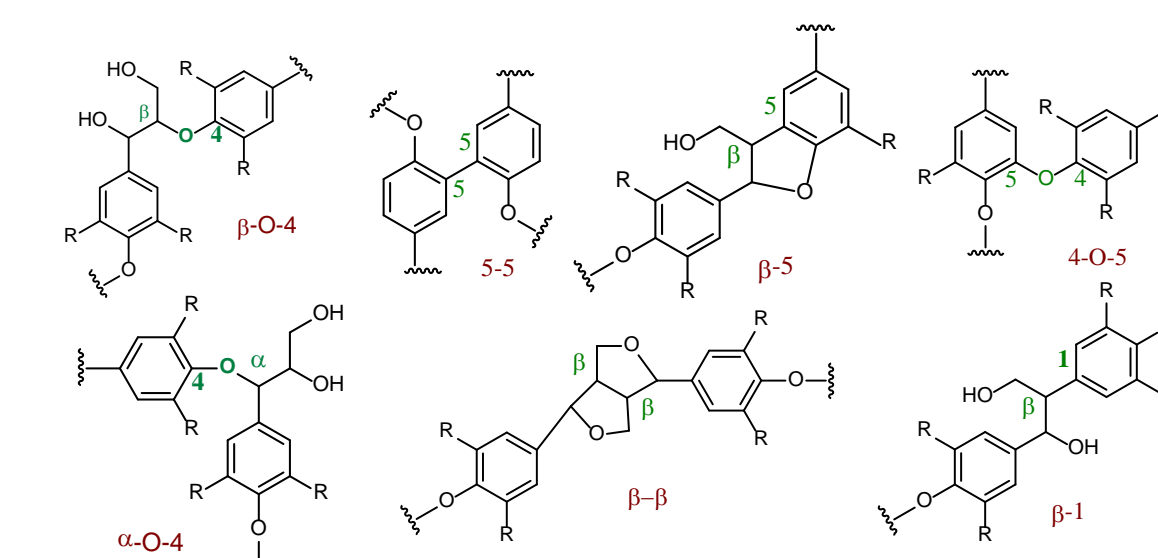


Figure 2. Type of bonds in lignin.

The complexity has led lignin to be treated as a waste stream, and typically burned to produce energy. However, lignin is a significant portion of the total carbon in biomass, and better use of this fraction is a requirement to improve the economic balance of any bio-refinery.

For this reason, research on upgrading lignin has become of recent interest, as many interesting products, mainly aromatics, can potentially be produced from lignin. Here we therefore present an overview conversion of lignin into chemicals using heterogeneous catalysis.

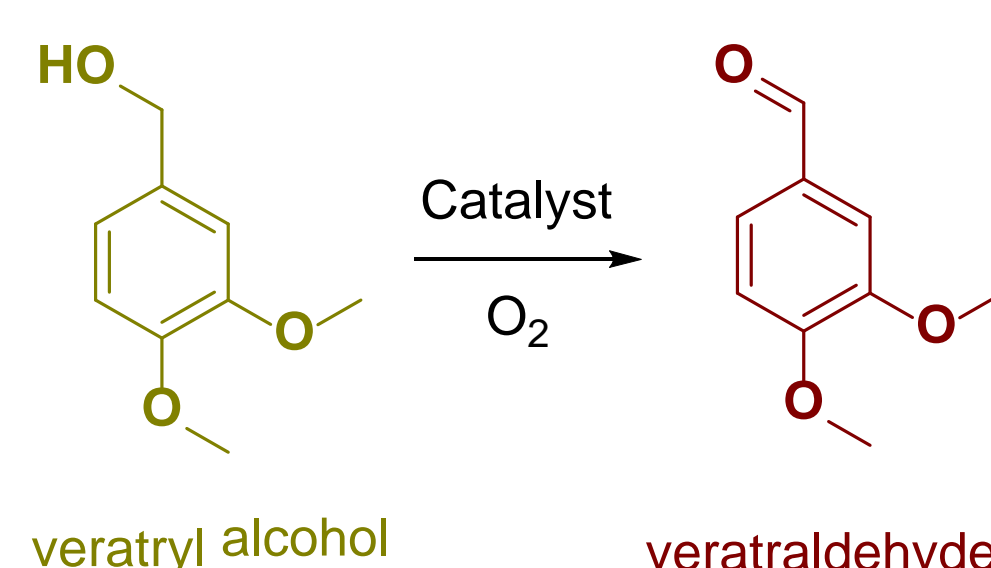
Experimental

Catalyst preparation

An appropriate amount of aqueous solution of ruthenium or manganese precursors was mixed with support (alumina or silica), dried and calcined at 450°C to get metal the corresponding supported metal oxide catalysts.

Catalytic reactions

A 50 ml autoclave (Microclave reactor from Autoclave Engineers) was charged with an appropriate amount of veratryl alcohol, catalyst (150 mg) and water as solvent (10 ml) and then pressurized with Air (5 bar). The autoclave was heated to 160°C and the stirring started once the temperature reached 140°C (300 rpm). After 5 h of stirring, the autoclave was quenched with cold water and analyzed by GC and GC-MS.



Results

Table 1. Data for Veratryl alcohol oxidation with different catalyst.

CATALYST	BET surface AREA (m ² /g)	Veratryl alcohol CONVERSION (%)	Veratraldehyde YIELD (%)
Ru/Al ₂ O ₃	166	93	67
Ru/SiO ₂	422	96	46
Mn/Al ₂ O ₃	152	69	17
Al ₂ O ₃	204	46	3
SiO ₂	472	59	3
Blank	-	34	2

Table 2. Data for Veratryl alcohol oxidation in different solvent testing

SOLVENT	Veratryl alcohol CONVERSION (%)	Veratraldehyde YIELD (%)
Methanol	56	1
Water	93	67

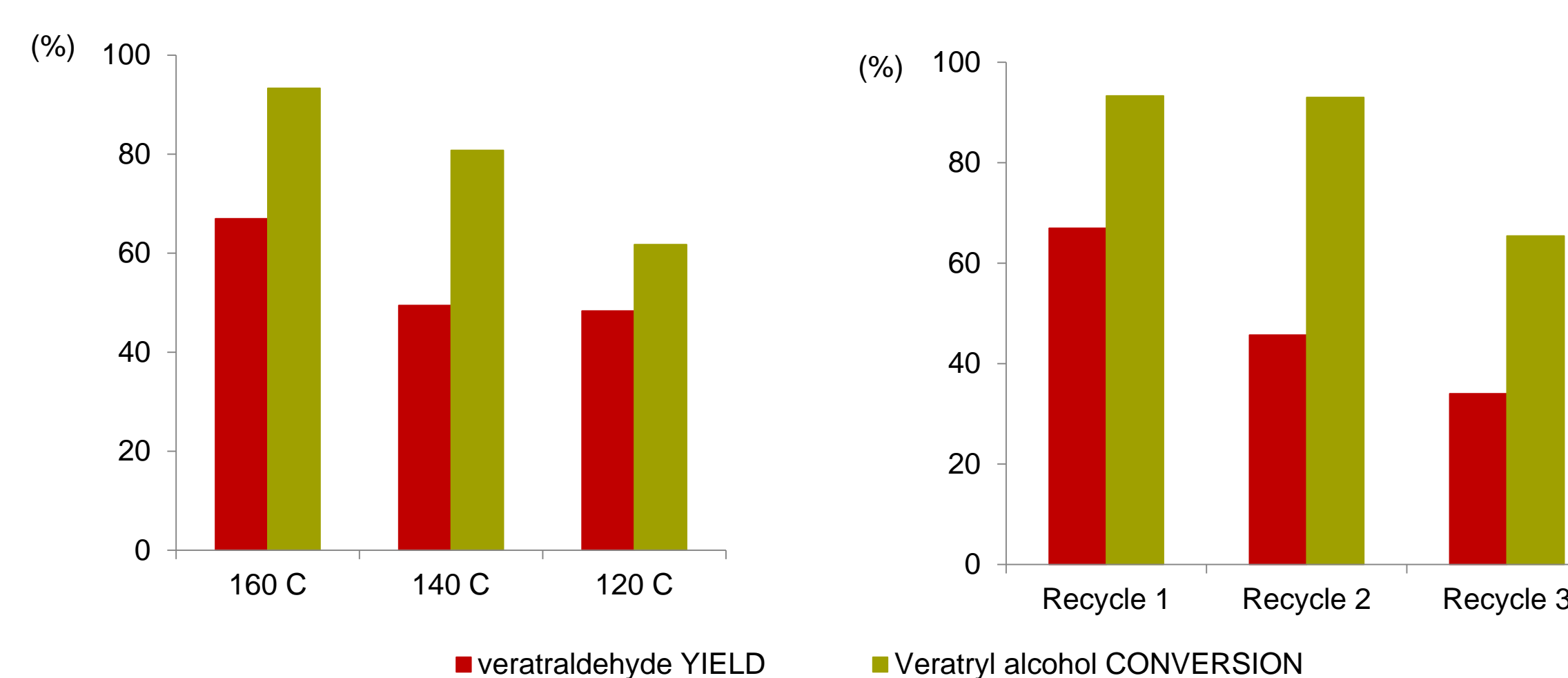


Figure 3. Temperature study using Ru/Al₂O₃ in 5 h reaction

Figure 4. Time-course study on the conversion of veratryl alcohol over Ru/Al₂O₃ in 5 hours

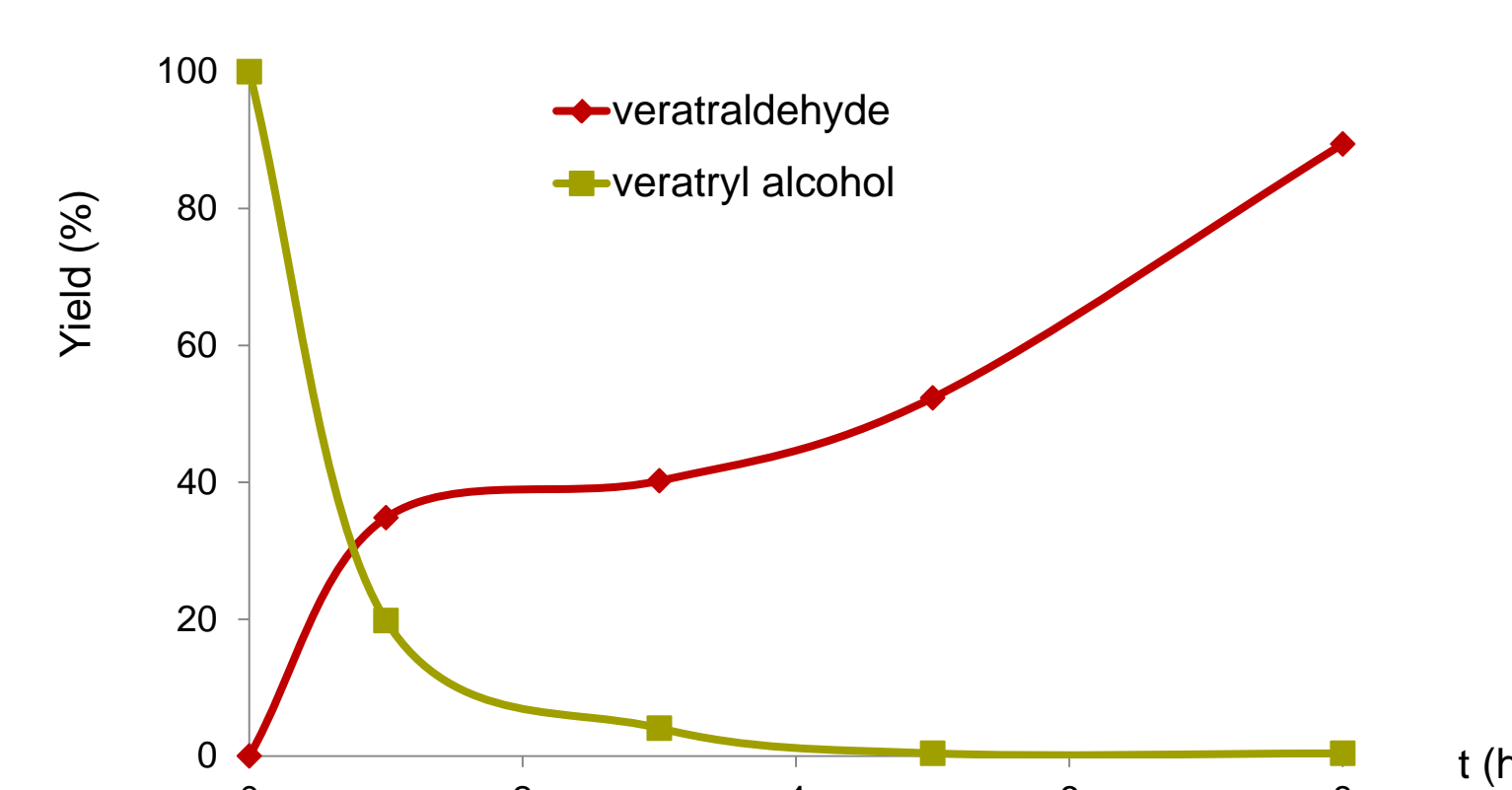


Figure 5. Time-yield study over Ru/Al₂O₃.

Conclusion

Time-course study revealed that 8 hours of reaction time required to get an optimum yield towards veratraldehyde.

Temperature study shows that at 160 °C the veratraldehyde yield is higher with 67 %, than at 140 °C or 120 °C which give yields of 50% and 48% respectively.

Among the catalyst employed, Ru/Al₂O₃ gave a highest yield to veratraldehyde (67 %) along with 93 % conversion of veratryl alcohol. However, Ru/SiO₂ also gave a comparable yield of veratraldehyde.

Ru/Al₂O₃ can be recyclable, however the yield of veratraldehyde decrease significantly.

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